

Collapse of poly(methacryloylethyl trimethylammonium methylsulfate) on addition of acetone into an aqueous solution

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Abstract

The effect of the solvent composition on the conformation of a super high molar mass polyelectrolyte, $M_w = 22\text{--}25 \times 10^6$, dissolved in a water–acetone mixture was investigated using static and dynamic light scattering. When increasing the concentration of acetone above 80 mass percent, a reversible conformational change of macromolecules occurs, which causes a sharp decrease in the viscosity, a rise in the light scattering intensity, and also a decrease in the radius of gyration, R_g , the hydrodynamic radius, R_h , as well as in the second virial coefficient A_2 . The correlation function measured by dynamic light scattering changes from bimodal to unimodal indicating the formation of compact globular structures. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymer coils dissolved in a good solvent shrink when a certain amount of nonsolvent is added into the solution. A coil-to-globule transition of polyacrylamide, PAAm, occurs in a water–acetone mixture during titration of the solution with acetone [1]. The difference in the refractive indices of water and acetone is small and, thus, water–acetone mixtures may be regarded as isorefractive systems. This assumption simplifies the use of light scattering to study the polymer conformation [1,2]. A similar conformational transition takes place in aqueous solutions of PAAm if methanol is used instead of acetone [3].

Qualitatively, the collapse of macromolecules in solvent–nonsolvent mixtures is well understood. Addition of the precipitant changes a thermodynamically good solvent into a poor one. A sudden contraction of the polymer coils occurs when the concentration of the precipitant reaches a certain critical value. In aqueous systems the situation is complicated; an organic precipitant tends to dissolve the hydrophobic parts of the polymer and leads to the segregation of hydrophobic and hydrophilic parts. Micelle shaped polymer globules may form in such mixtures. The polymer–

solvent interaction is even more complicated in aqueous polyelectrolyte solutions. However, one can expect the existence of charges preventing the aggregation of the polymers, which makes it possible to follow the transition also in fairly concentrated solutions using various research methods [4]. The size of a polyelectrolyte globule may be bigger than that of uncharged molecules with equal molar mass. Only a few experimental studies have been devoted to the coil–globule transition of polyelectrolytes.

The balance of hydrophobic and hydrophilic interactions in polyelectrolyte systems may be changed by the addition of various reagents. For example, a phase transition of DNA in an aqueous solution has been induced by polyethylene glycol, polyamines, multivalent metal cations, as well as a cationic surfactant. A particular region in which coils and globules coexist, was found in the phase diagram by Yoshikawa, Khokhlov and co-workers using fluorescence microscopy [5–7].

Polymer systems with strong interactions, such as the solutions of polyelectrolytes in mixed solvents, are a topic of intensive theoretical research. A toroidal globule [7] as well as necklace-like structures with compact beads joined by narrow strings [8] have been suggested as models of the polyelectrolytes in a poor solvent.

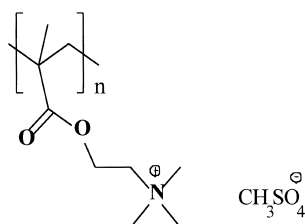
In our previous reports it has been shown that synthetic high molar mass polyanions and polycations may undergo a conformational transition induced by the change in the

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solvent composition [4,9–11]. The mass fraction of acetone as a precipitant γ , was varied in the solvent mixtures. An abrupt decrease in the viscosity as well as in the conductivity of the solutions, particle size, second virial coefficient A_2 , and the coil dissymmetry parameter occurs in a narrow range of γ .

In this paper, the conformational transition of a high molar mass polycation poly(methacryloylethyl trimethylammonium methylsulfate), PMETMMS, will be discussed. The viscosity of PMETMMS during the coil-to-globule transition has already been reported [11]. The polymer has the following structure:



It has been shown that by changing the solvent composition, at γ about 0.80 the size of the polymer changes non-linearly. The radius of gyration of the polymer with $M_w = 25 \times 10^6$ was about 50 nm in a collapsed state. However, the process of the formation of the polyelectrolyte globule was unclear [11].

In this report, the results of static and dynamic light scattering measurements on PMETMMS dissolved in mixtures of water and acetone are presented. The measurements were done to study the mechanism of the conformational change. Special attention has been paid to the kinetics of this process. The possible structure of PMETMMS globule is also discussed.

2. Experimental

2.1. Materials

Three samples of poly(methacryloylethyl trimethylammonium methylsulfate), PMETMMS, were synthesised by free-radical polymerisation using a twice precipitated monomer and a Co(III) salt as the initiating system [12]. The monomer was prepared by quaternising a commercial monomer, dimethylaminoethyl methacrylate (purchased from Yarcintez, Yaroslavl, Russia), with dimethyl sulfate. PMETMMS was examined using static light scattering, SLS, in an 1 M aqueous sodium nitrate solution, where the polyelectrolyte effect is totally suppressed. This data was compared with values of M_w obtained for the polymer dissolved in water–acetone mixtures. The acetone fractions were close to $\gamma = 0.82$, in which fraction the conformational change is known to occur. The molar masses of PMETMMS samples have been measured also by sedimentation–diffusion. Good agreement of both methods indicates the narrow molar mass distribution of the samples studied. According

to a sedimentation–diffusion analysis the polydispersity of samples was $M_z/M_w = 1.15–1.20$; assuming a Schulz distribution $M_w/M_n = 1.6–1.8$.

2.2. Instrumentation

In the previous reports, samples of PMETMMS were characterised using a Sofica photogoniometer (546 nm wavelength). This paper deals with a further analysis of the same samples using Brookhaven Instruments BI-200SM Goniometer and a BI-2030AT digital correlator, BIC. A laser (Spectra Physics SP127-35) operating at 632.8 nm wavelength was used as the light source (power 35 mW). The SLS data were treated using Zimm's double extrapolation method. Specific refractive index increments of the polymer, dn/dc , dissolved in various water–acetone mixtures are equal within the experimental error. The value 0.166 ml/g, measured using a WYATT/OPTILAB 903 interferometric refractometer operating at wavelength 632.8 nm, was used. The experiments show that the values of M_w were not affected by selective sorption. Most of the correlation functions measured by dynamic light scattering, DLS, were recorded in the real-time multi-tau mode. The shortest sample time was changed from 5 to 30 μ s. The correlator uses 136 data channels. The solutions were purified of dust particles by centrifugation at 6000 rpm for 90 min. All measurements were done at 20°C. Water was deionised with ELGASTAT UHQ-PS device. HPLC grade acetone from Labscan Ltd was used.

3. Results and discussion

3.1. Static light scattering

The conformational transition of the polymer was studied by the following procedure. An aqueous stock solution of PMETMMS was titrated at room temperature with acetone during 10 hours to get a solution with $\gamma = 0.74$. The solution, with $\gamma = 0.74$ and the polymer concentration $c = 0.022$ mg/ml was allowed to equilibrate for 48 h. Then, this solution was titrated with acetone through the transition region. In the end of the titration, γ was 0.85 and the polymer concentration 0.013 mg/ml. Fig. 1 represents the change in the light scattering intensity at 90° angle as a function of the solvent composition γ for PMETMMS-1 (see Table 1). The difference in the light scattering intensity between the solution and the solvent, $I - I_0$, is given in counts of photons per second. Curves 1 and 3 in Fig. 1 were measured after checking that the system is at equilibrium. The time dependence of the scattered light intensity was used as a criterion of stability: after each addition of acetone into a solution with certain γ , the intensity increases but reaches a constant value in 5–6 h. As may be seen in Fig. 1, during the titration from $\gamma = 0.74$ to 0.85 the angular dissymmetry parameter $Z = I^{45}/I^{135}$ changes from 3.7 to 1.5

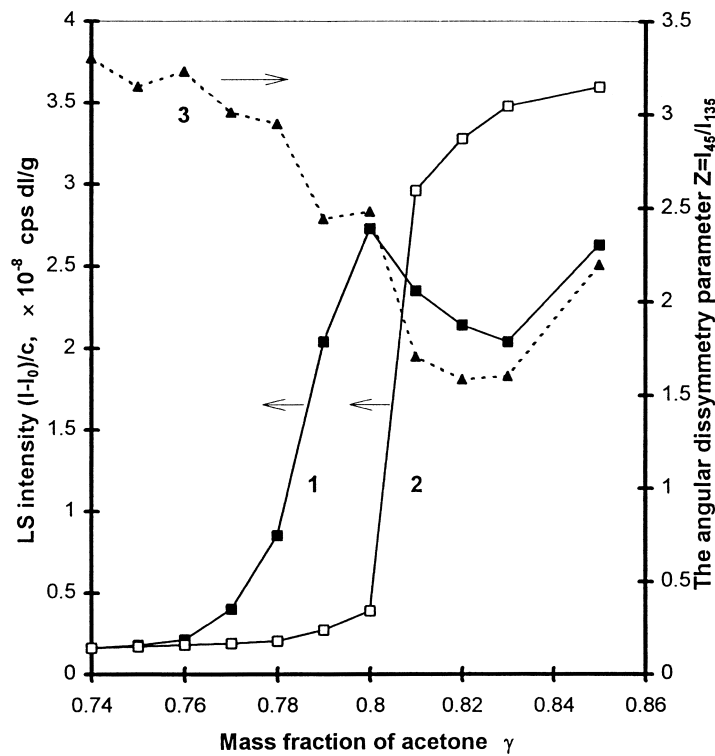


Fig. 1. The dependence of the reduced intensity of scattered light, $(I - I_0)/c$, for water–acetone solutions of PMETMMS-1 at an angle 90° (1 and 2), and the angular dissymmetry parameter Z on γ (3). The intensity is given in counts of photons per second, cps. The polymer concentration is $c = 0.022$ mg/ml, when $\gamma = 0.74$. Curves 1 and 3 correspond to an equilibrium transition.

while the intensity increases. The growth of the intensity is related to the decrease of the second virial coefficient. At a certain value of γ , the macromolecules adopt compact structures and the growth of the intensity stops. When $\gamma > 0.82$ the intensity of the scattered light starts to increase again, owing to the aggregation of the polymers. Curve 2 in Fig. 1 was produced by measuring the intensity 10 min. after each addition of acetone. In this case, equilibrium was not attained and the transition is more pronounced than that represented by curve 1. Also, in curve 2 the transition occurs at a higher value of γ . Evidently, during a fast titration the aggregation process is more probable because of an uneven distribution of acetone in the solution. Therefore, equilibrium titration was chosen for further experiments.

The interpretation of the experimental data obtained by SLS is complicated when γ is less than 0.80 due to strong intermolecular interactions and polyelectrolyte effects. In

this region of γ the values of the second virial coefficient are very high. The molecular parameters can be reliably determined only near the region of the conformational transition. In the transition region $0.80 < \gamma < 0.82$ A_2 becomes equal to zero and even less than zero indicating that transition occurs in a poor solvent. A summary of the SLS measurements is presented in Table 1. For comparison, the results obtained using a Sofica instrument are also shown (data from Ref. [11]). The results obtained for Sample 1 were chosen to be presented as an example of PMETMMS behaviour in the transition region. Zimm plots for PMETMMS-1 dissolved in an aqueous salt solution and a water–acetone ($\gamma = 0.82$) mixture are presented in Fig. 2.

The polymer concentration was varied from 0.1 to 0.01 mg/ml in the salt solutions and from 0.03 to 0.003 mg/ml in the water–acetone mixtures. The approximate overlap concentration, c^* , can be calculated as for

Table 1
Static light scattering results of three samples of PMETMMS, measured with two instruments (see Section 2)

	Sofica 1 M NaNO ₃			BIC 1 M NaNO ₃			$\gamma = 0.82$		
	$M_w \times 10^{-6}$ [g/mol]	$M_w \times 10^{-6}$ [g/mol]	A_2	$M_w \times 10^{-6}$ [g/mol]	R_g [nm]	$A_2 \times 10^4$ [cm ³ mol/g ²]	$M_w \times 10^{-6}$ [g/mol]	R_g [nm]	$A_2 \times 10^4$ [cm ³ mol/g ²]
Sample 1	22	23	≈ 0	21.6	235	0.17	26.4	52.4	-0.45
Sample 2	24	23	≈ 0	25.8	258	0.08	23.4	57.1	-0.29
Sample 3	25	25	≈ 0	26.1	248	0.23	27.0	53.2	-0.33

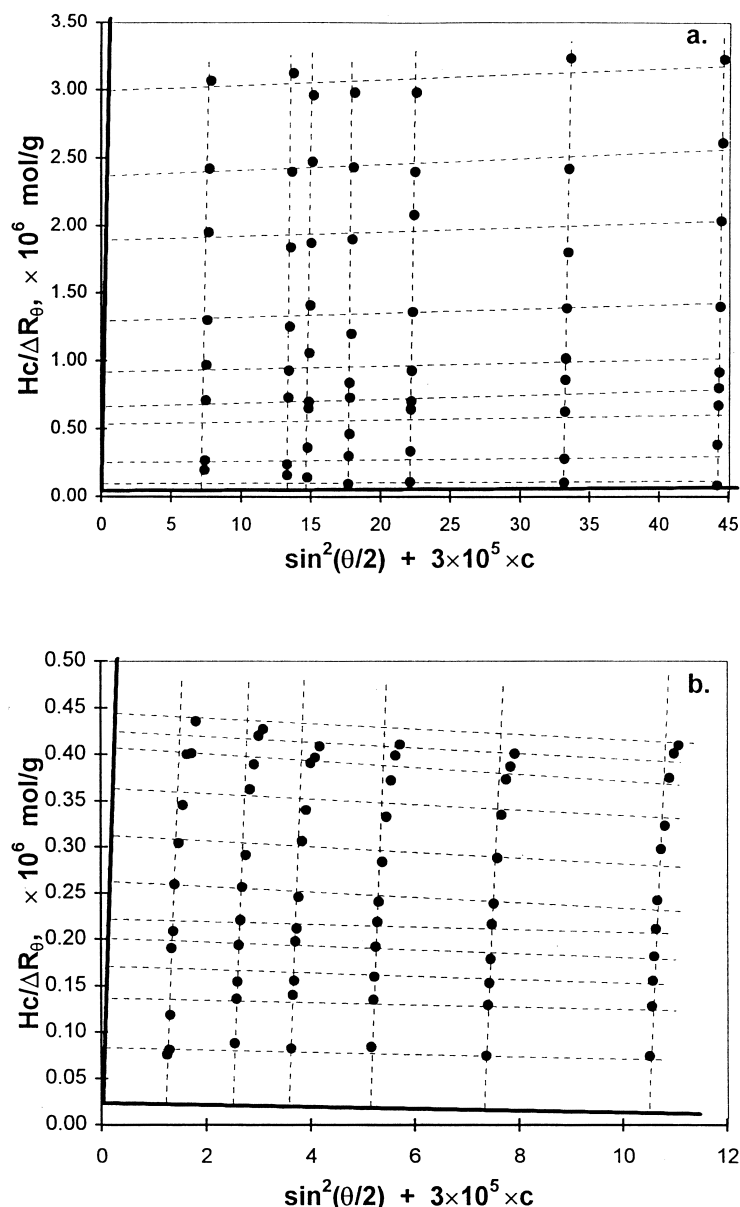


Fig. 2. Zimm plot for PMETMMS-1 dissolved in aqueous 1 M NaNO₃ (a) and in a water–acetone mixture with $\gamma = 0.82$ (b). H is the optical constant, R_{θ} is the Rayleigh factor, and c is the polymer concentration, given in mg/ml.

uncharged polymer coils by

$$c^* = M_w / [N_A (4\pi/3) R_g^3]. \quad (1)$$

For PMETMMS-1 the values of c^* are 0.66 and 77 mg/ml in an aqueous saline solution and in a water–acetone mixture with $\gamma = 0.82$, respectively. This shows that all the measurements were done in a region of dilute solutions.

It should be emphasised that the molar masses of PMETMMS determined in an aqueous saline solution and in the water–acetone mixture are equal. The data convincingly demonstrates that the conformational change occurs on a molecular level. On the other hand, this is an experimental evidence of the isorefractive character of the water–acetone solutions.

The transition is completely reversible. The polymer

molecules have a compact conformation when γ is 0.82. The size of the polymer in an aqueous salt solution, in which the polyion charge is completely screened, is larger than the size of the molecules at $\gamma = 0.82$. When $\gamma > 0.85$, a slow aggregation is observed as increasing values of M_w and $\langle R_g^2 \rangle^{1/2}$.

Since PMETMMS does not dissolve in acetone the macromolecules adopt a globular structure. This structure is unusual and differs from globules of uncharged polymers. It has been shown [11] that the decrease in the solution conductivity is related to a decrease in the degree of dissociation and counterion condensation. In media of low dielectric constant polyelectrolytes are known to form ion-pairs which attract one another leading to a collapse of the polyion chains [13]. However, a small amount of charges

still remains on PMETMMS owing to the reorientation of hydrophobic and hydrophilic parts [11]. The structure of the water–acetone mixture inside and outside of the polymers may also change, as is known to happen when micelles are formed in mixed solvents. As a result, the macromolecules retain their solubility in water–acetone mixtures with $\gamma > 0.80$.

It is interesting to compare the critical value of γ for PMETMMS with the value reported for uncharged PAAm [1,2]. The coil-to-globule transition of PAAm occurs in mixtures with the mass fraction of acetone $\gamma = 0.27–0.30$. Close to this value ($0.30 < \gamma < 0.40$) the water–acetone mixture is known to show certain singularities, i.e. a maximum in viscosity as well as in conductivity.

3.2. Dynamic light scattering

In the dynamic light scattering experiments, the time autocorrelation function of the scattered intensity $G_2(t)$ was measured with homodyne method. The function has the form

$$G_2(t) = \langle I(0)I(t) \rangle. \quad (2)$$

This function may be converted into a correlation function $G_1(t)$ of the scattered electric field using Siegert's relationship

$$G_2(t) = G_2(\infty)[1 + G_1(t)], \quad (3)$$

where $G_2(\infty)$ is the experimentally determined baseline. In a normalised form

$$g_2(t) = 1 + \beta |g_1(t)|^2, \quad (4)$$

where $g_2(t) = G_2(t)/G_2(\infty)$, $|g_1(t)| = [\beta^{-1}G_1(t)]^{1/2}$, and β is

the coherence factor determined by the geometry of the detection. In our case $0.5 \leq \beta \leq 0.8$. At $qR_g < 1$ or for structureless particles without internal motions, the normalised characteristic line-width distribution $G(\Gamma)$ can be evaluated by performing the Laplace inversion:

$$|g_1(t)| = \int_0^\infty G(\Gamma)e^{-\Gamma t} d\Gamma \quad (5)$$

with average characteristic line-width

$$\langle \Gamma \rangle = \int \Gamma G(\Gamma) d\Gamma = Dq^2. \quad (6)$$

D is the average translation diffusion coefficient. For molecular size distribution analysis the CONTIN program was used [14]. When $qR_g > 1$, the scattering function becomes more complicated, e.g. because of the contribution of internal motions.

DLS measurements were performed through the whole region of conformational transition. When γ is less than 0.74 there are very strong intensity fluctuations of scattered light which make the measurements difficult, especially with low angles. Therefore, the 90° angle of detection was chosen for the analysis of the conformational change.

Fig. 3 shows the correlation functions for the PMETMMS-1 corresponding to the curve 1 in Fig. 1 (equilibrium titration). In order to present measured correlation functions $G_2(t)$ in more suitable form we used following normalisation procedure

$$|G_2(t)| = \frac{G_2(t) - G_2(\infty)}{G_2(0) - G_2(\infty)}. \quad (7)$$

With $\gamma < 0.80$ two relaxation processes are distinguished.

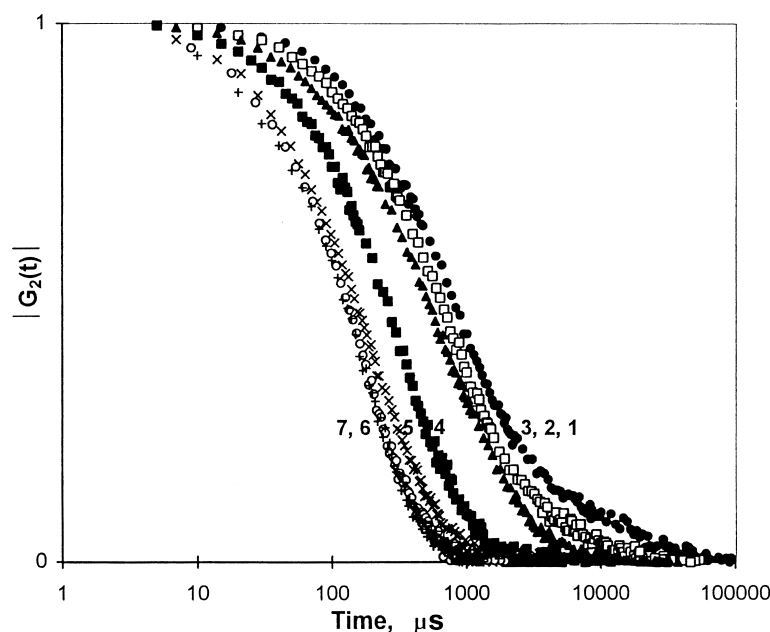


Fig. 3. Correlation functions for PMETMMS-1 dissolved in water–acetone solutions with varying mass fraction of acetone: (1) 0.74, (2) 0.76, (3) 0.77, (4) 0.78, (5) 0.79, (6) 0.80, (7) 0.82. The polymer concentration is 0.022 mg/ml when $\gamma = 0.74$.

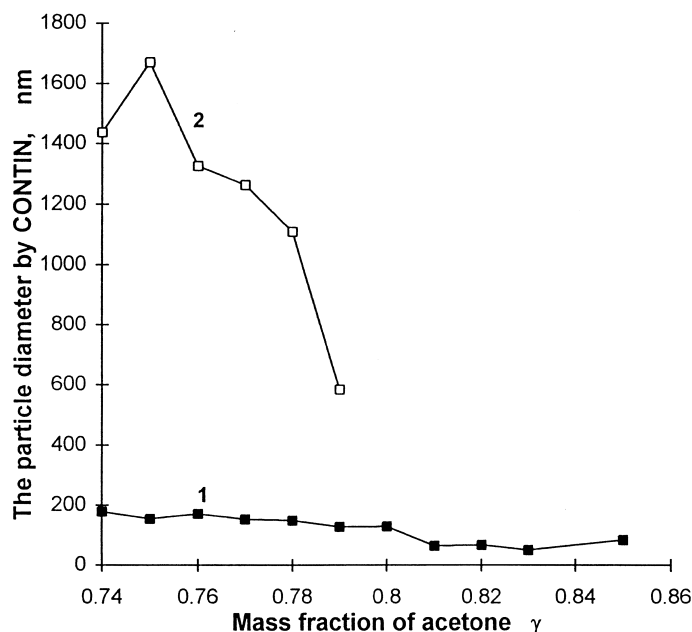


Fig. 4. The dependence of the apparent particle sizes on γ calculated with CONTIN from the correlation functions in Fig. 3. Curve 1 refers to the fast mode and the curve 2 to the slow one.

When γ increases the contribution of the slow mode decreases, up to $\gamma = 0.80$ where only the fast mode is observed. The shape of the correlation function changes noticeably in the region $0.77 < \gamma < 0.79$. With further titration of the solution the short relaxation time decreases continuously up to $\gamma = 0.82$. For $\gamma > 0.82$ no more changes in the short relaxation times were observed. The molecular size analysis of the correlation functions is shown in Fig. 4.

The correlation function is bimodal, if it is measured immediately after addition of acetone into a solution with $\gamma < 0.82$ to get a solution with $\gamma > 0.82$. The fast mode corresponds to the particles of the same size as those in a compact conformation. Gradually the system reaches equilibrium and the correlation function becomes monomodal indicating that only the small particles exist.

The angle dependence was studied for three solutions

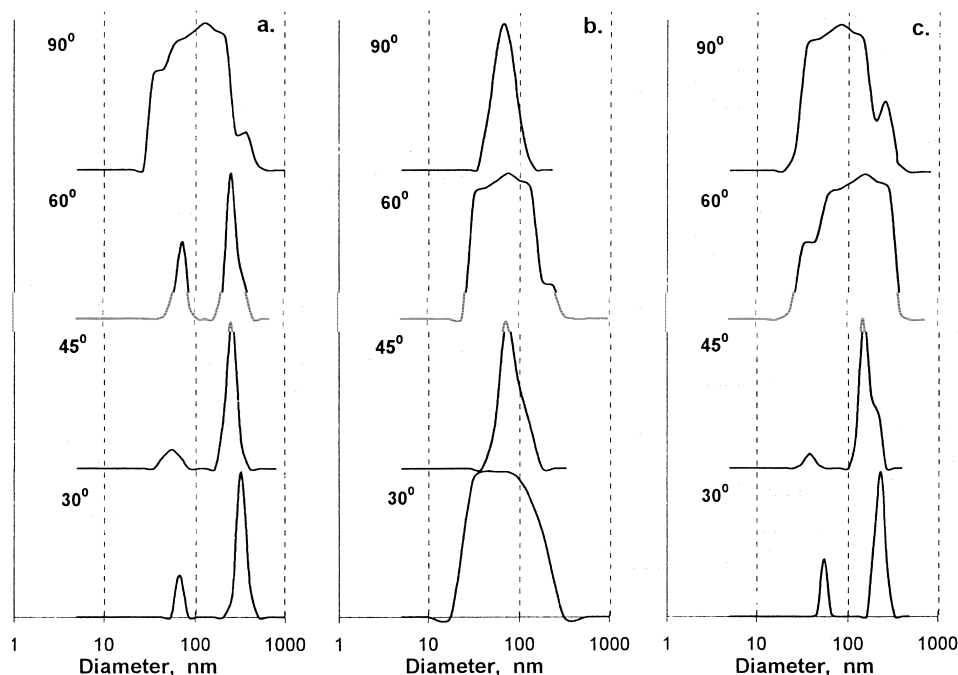


Fig. 5. Angle dependence of the size distribution of PMETMMS-1 dissolved in water–acetone mixtures with γ equal to 0.80 (a), 0.82 (b), and 0.85 (c). The polymer concentration is 0.013 mg/ml.

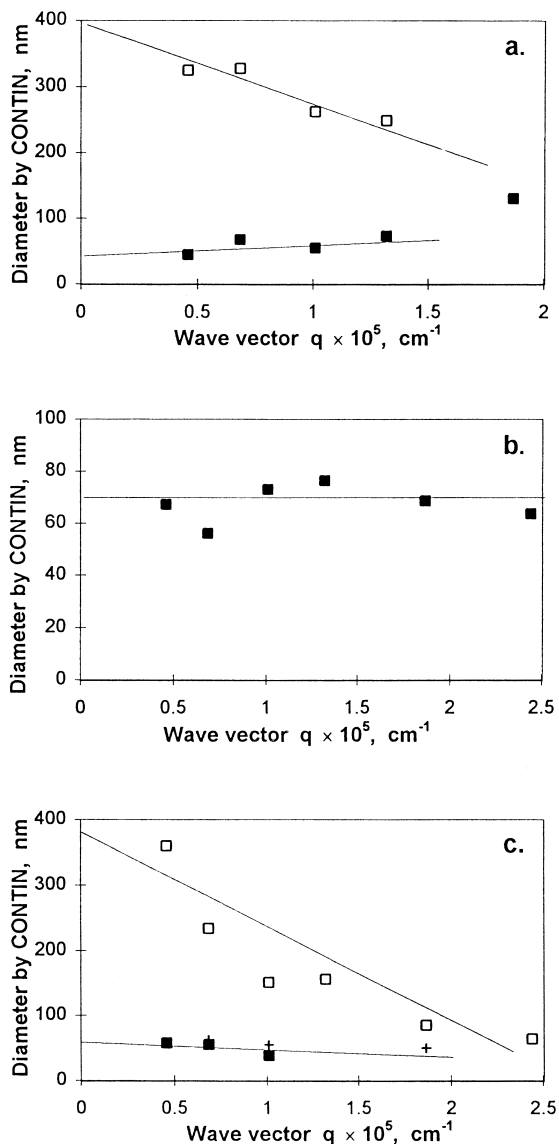


Fig. 6. Angle dependence of the average particle size of PMETMMS-1, data from Fig. 5. Crosses present the solutions without aggregates.

with varying γ , but equal polymer concentration, 0.013 mg/ml (see Figs 5 and 6). When γ equals 0.80, the CONTIN program does not distinguish two modes of the correlation function at 90° ($qR_h \geq 1.2$). With smaller angles, however, a bimodal distribution is observed. Molecular size distribution becomes unimodal when $\gamma = 0.82$ ($0.6 < qR_h < 0.2$). It is well seen that in such a system there is no angle dependence of the hydrodynamic size.

The origin of the slow mode detectable in the correlation function at $\gamma < 0.82$ is not clear. The value of the slow diffusion coefficient varies strongly and depends on many factors. The bimodality of the correlation functions of polyelectrolyte solutions without added salt is nowadays widely discussed. It could be due to the presence of super-molecular structures caused by strong intermolecular interactions. This is not the case because if such structures existed, the

contribution of the slow mode should increase with an increase of γ from 0.74 to 0.82. However, an opposite behaviour is observed, and the slow mode disappears at $\gamma = 0.82$. The existence of the slow mode may also owe to intensity fluctuations due to the interaction of the polymer coils in semidilute solutions, even at very low polymer concentration [15]. Topp et al. have studied quaternised poly(2-vinylpyridine) in aqueous solution with low salt concentration. These authors showed clearly the dependence of the bimodal shape of the correlation function on the charge density of the polymer [16]. Yoshikawa concluded [5] that for DNA, coils and globules coexist in the transition region which may be the case also in the present system. The size of PMETMMS particles corresponding to the slow mode are comparable with the size of the polymer coils in an aqueous salt solution.

After the transition, the polymer does not immediately precipitate and the system is quasistable. With increasing γ above 0.85 a slow diffusion process is occasionally (but not always) observed due to aggregation. The appearance of the aggregates depends on several factors like the age of the solution, the way of the preparation of the solution, as well as on the purity of the solvent. Fig. 6 shows the angle dependence of the size of the diffusing entities with varying value of γ . In Fig. 6(c) the data from the solutions without aggregates are also presented. In those cases the formation of aggregate particles was not detected even after ageing for 48 h or with further addition of acetone up to $\gamma = 0.95$.

Extrapolation to the zero angle shows that the size of compact structures in a solution with $\gamma = 0.82$ is $R_h = 35$ nm, whereas $R_g = 52.4$ nm. The average density of the polymer in its collapsed state was calculated assuming a regular distribution of the mass inside a sphere of radius R_h or R_g , using a simple approximation $\rho \approx M_w/[N_A \cdot \frac{4}{3}\pi R^3]^{-1}$. The van der Waals' volume of PMETMMS, V_w , was also calculated and compared with the volume occupied by the molecule in a collapsed state, $\phi = V_w/V_h \times 100\%$, see Table 2. It is concluded that PMETMMS in a compact state still contains a considerable amount of solvent. The change of the balance of hydrophobic and hydrophilic interactions in polyelectrolytes dissolved in aqueous-organic solvent may result in a difference of the solvent composition inside and outside of the coils [6] and lead to micelle-like structures. For an accurate analysis of the polymer density one should know the detailed structure of the collapsed polyelectrolyte globule.

For the uncharged polymers listed in Table 2, the ratio R_g/R_h is close to 0.77 which corresponds to a solid isotropic sphere. For collapsed PMETMMS the ratio R_g/R_h is 1.50. Flow birefringence measurements have shown that during the transition the conformation of PMETMMS changes from a Gaussian coil into a symmetrical particle without the macroform effect [4]. Thus, the results show that the structure of the polyelectrolyte globules differs from the structure of the globules of uncharged polymers.

Table 2
Characteristics of certain nonpolar and polar polymers in the collapsed state

Polymer	$M_w \times 10^{-6}$	Solvent	Variable	Size of globule [nm]	R_g/R_h	$\rho,^d$ [g cm ⁻³]	ϕ [%] ^e	Ref.
Polystyrene	26	cyclohexane	temperature	$R_g \approx 41$ $R_h \approx 55$	0.74	-	-	[17]
Polystyrene	8.6	cyclohexane	temperature	$R_h \approx 23.2$	-	-	24-40	[18]
Polystyrene	2	dioctyl phthalate	temperature	$R_g < 15$	-	-	-	[19]
Branched PAAm	30	water-acetone	temperature	$R_g = 36$	-	0.30	-	[2]
PNIPAAm ^a	10.8	water	solvent composition	$R_g \approx 20$ $R_h \approx 32$	0.62	0.20	20	[20]
PNIPAAm ^a	7	water + SDS ^b	temperature	$R_g \approx 16.0$ $R_h \approx 19.8$	0.81	0.36	-	[21]
T4DNA	108	water	Co(NH ₃) ₆ Cl ₃	apparent mean R of toroid 45	-	-	-	[7]
Na-PAAMPS ^c	3.6	water-acetone	solvent composition	$R_g \approx 10$ $R_h \approx 9.4$	1.06	-	64	[9]
PMETMMS	26.4	water-acetone	solvent composition	$R_g = 52.4$ $R_h = 35$	1.50	0.07 0.24	12	

^aPoly(N-isopropylacrylamide).

^bSodium *n*-dodecyl sulfate.

^cSodium poly(2-acrylamido-2-methylpropane sulphonate).

^dDensity.

^e $\phi = V_w/V_h \times 100\%$, see text.

The values of R_h are those measured from dilute solutions. The diffusion coefficient is known to have strong concentration dependence in good solvents:

$$D = kTf^{-1}(c)(1 + 2A_2M_w c), \quad (8)$$

where $f(c)$ is a friction coefficient. In the present case $A_2 \approx 0$ when $\gamma = 0.82$. Generally, $f(c)$ is almost concentration independent and the measured values of R_h were assumed to be very close to the values at infinite dilution. However, the concentration dependence of the diffusion coefficient of PMETMMS globe needs to be studied more closely.

4. Conclusions

PMETMMS molecules with $M_w 22 \times 10^{-6}$ have been shown to take a very compact conformation when $\gamma > 0.82$. For the compacted polymer, $R_h = 35$ nm and $R_g = 52$ nm. The conformational transition occurs owing to the change in the hydrophobic and hydrophilic interactions when adding acetone into an aqueous polymer solution. Values of A_2 are less than zero and show that the water-acetone mixture with $\gamma > 0.82$ behaves like a poor solvent. A toroidal structure of PMETMMS, similar to DNA [5–7], as well as a spherical flow-through structure with heterogeneous density distribution [8] can be suggested as hypothetical models describing the compact conformation.

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